

PATENT SPECIFICATION



825,872

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COMPLETE SPECIFICATION

DRAWINGS ATTACHED

Improvements in or relating to the Electrolytic Production of Magnesium

I, ICHIRO EGAMI, a Japanese subject, of No. 150, 3-chome, Shinden-cho, Ichikawa, Chiba, Japan, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an improved method for the electrolytic production of magnesium, and to apparatus for carrying it out.

It is well known that metallic magnesium may be prepared by the direct current electrolysis of a mixture of magnesium chloride and sodium chloride at about 750°C using a graphite anode and iron cathode. In this process, the main raw material, that is magnesium chloride, is replenished as it is consumed by the electrolysis.

It has already been proposed to use a special electrode instead of the graphite electrode commonly used in the above process which electrode consists of a mixture of magnesium oxide and a carbonaceous substance which has been baked. With use of this kind of baked electrode, chlorine gas generated during the electrolysis will react with magnesium oxide contained in the electrode to form magnesium chloride. In this way, the consumed magnesium chloride can, in theory, be automatically replenished as the electrolysis proceeds and the process may be carried out in a continuous manner, if the baked electrode is replaced as it is used up. In this process, a mixture of carbon dioxide and carbon monoxide is liberated at the anode, while molten magnesium is liberated at the iron cathodes and rises to the surface of the bath on account of its smaller specific gravity.

The above process has certain advantages amongst which may be mentioned the following:—

[Price 3s. 6d.]

1. Lower unit cost of metallic magnesium produced because the need to replace the magnesium chloride consumed by the electrolysis from an outside source is substantially obviated.
2. The necessity for treating the gas liberated by the electrolysis for removal of chlorine is avoided because the chlorine gas generated combines with the magnesium oxide in the anode.
3. Ease and convenience in operation, reduction in labour and welfare costs and elimination of waste-gas troubles, resulting from the fact that the issuing gases consist substantially of CO and CO₂, while the chlorine-gas once generated is almost quantitatively re-utilized by the process itself.
4. Higher thermal efficiency because of the formation of magnesium chloride at the bath temperature, while in known processes the chloride is generally produced in a separate chlorination furnace and the cooled product is then supplied to an electrolytic furnace, in which it must be heated to the desired temperature, thus resulting in higher thermal losses.

In the above process, using a special baked electrode, the consumed electrode should be exchanged for or connected to a new one, as it is consumed in the continuous operation. It is difficult, however, to accomplish a highly conductive, direct connection between the baked electrodes. If the consumed electrodes are exchanged for new ones, instead of employing direct connections between the new and the old electrode, the total amount of unconsumed, waste electrodes, would be rather considerable, so that the economical balance in this case would become more unfavourable.

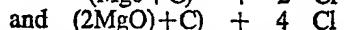
It has also been proposed to feed a paste-like mixture of a magnesium

compound and carbon-containing material into a vertical metal anode cylinder provided with a perforated bottom plate such that the molten salt in the electrolytic bath is able to contact the paste-like mixture through the perforations and the chlorine generated in electrolysis to attack the magnesium compound in the paste. This procedure, although overcoming some of the above disadvantages, is often difficult to operate in continuous production due to rapid wear of the anode cylinder and, in particular, of the perforated bottom plate, which thus has frequently to be replaced, thereby interrupting production.

An object of this invention is to provide an improved method for the electrolytic production of magnesium, and apparatus for carrying out the method, in which an anode comprising magnesium oxide and a carbonaceous material is fed into a metal anode shell, both the shell and the paste being readily replenished in use, thus substantially reducing the disadvantages referred to above.

According to the invention I provide a method for the electrolytic production of magnesium by the electrolysis of a fused mixture comprising magnesium chloride and alkali metal and/or alkaline earth metal halides, in which the anode comprises a paste-like mixture of a carbonaceous substance and a magnesium compound capable of reacting with the chlorine formed in the electrolysis said paste-like mixture being surrounded by a metal shell, both the paste-like mixture and the metal shell being built up from above as the anode is consumed from below by the electrolytic process.

According to a feature of the invention I also provide electrolytic apparatus for carrying out the above method comprising an electrolytic furnace, a cathode and an anode, in which said anode comprises a paste-like mixture of a carbonaceous substance and a magnesium compound capable



For continuous operation, the magnesium oxide and the carbonaceous substance in the paste must be replenished as they are consumed, but it is virtually unnecessary to add any magnesium chloride as such to the electrolytic bath as the replacement of the magnesium results from the reaction of the nascent chlorine with the anode paste.

As the electrolysis of the fused salt proceeds, the anode paste is gradually and automatically baked to the desired degree. At the beginning of electrolysis it is necessary to insert an electrode which has already been baked and we have found it convenient for this purpose to use the electrolytic furnace itself for the prebaking of the paste mixture. Alterna-

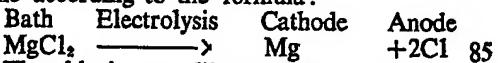
of reacting with chlorine liberated in the electrolysis, said paste-like mixture being surrounded by a metal shell, said shell being so constructed that it can be built up from above as it is consumed from below by the electrolytic process.

As magnesium compounds capable of reacting with chlorine may be mentioned magnesium oxide, in particular roasted magnesite, and magnesium hydroxide, while as carbonaceous substance pitch, tar, pitch oil, natural or artificial graphite, coke powder, charcoal powder or a mixture thereof may be employed. It is preferred that the ratio between the magnesium compound and the carbonaceous substance be within the range of, 1:3 to 3:1 by weight. When solid substances only are used for the material of the paste, it is desirable to add a proportion of oil to produce a paste of the consistency desired. Preferably the magnesium compound and the carbonaceous substance are thoroughly mixed together at a temperature between 170° and 230°C.

It is preferred to carry out the electrolysis at between 720-780°C. the composition of the fused mixture undergoing electrolysis preferably consisting of 30% magnesium chloride and 70% sodium chloride.

It is further preferred to carry out the electrolysis at a voltage of 10-20 volts and the anode current is preferably maintained at 0.2-1.0 amps/sq. cm.

On electrolysis the magnesium chloride contained in the electrolytic bath is decomposed into metallic magnesium and chlorine according to the formula:



The chlorine gas liberated at the anode is in a nascent state, and is therefore highly reactive, this reactivity being increased by the high temperature of the bath, so that it acts instantly upon the magnesium oxide in the paste to give magnesium chloride, as shown:—



tively, the prebaking may be carried out in a separate baking furnace if this is considered desirable.

In order that the invention may be more fully understood a preferred embodiment of apparatus for carrying out the invention will now be described, by way of illustration only, with reference to the accompanying drawings, in which:—

Fig. 1 is a diagrammatic side elevation of apparatus according to the invention, partly in section;

Fig. 2 is an end view of the apparatus shown in Fig. 1, partly in section;

Figs. 3 and 4 are respectively end and side views of the anode assembly of the apparatus shown in Figs. 1 and 2; and Fig. 5

is a perspective view of the inner lattice work to be arranged within the anode assembly shown in Fig. 4 for the purpose of reinforcement and electric conduction.

5 The illustrated equipment is designed for a capacity of 2,000 amp.

Referring to the drawings it will be seen that apparatus according to the invention comprises a metal shell adapted to surround the anode in the form of a rectangular anode box 1 of, for example, thin metal sheet 120 cm long, 50 cm wide, and having a cross-sectional area of 6,000 cm²; in operation this is charged with a paste-like mixture consisting of a magnesium compound and a carbonaceous substance. An outer frame assembly 2, which is not consumed in the electrolytic process, is provided for the anode box 1, which outer frame has four side members detachably secured together, e.g. by bolts, each of said side members consisting in turn of a plurality of strips again detachably secured together. Iron is normally employed from the view point of cost as material for the anode box 1, but other materials, such as aluminium, magnesium or alloys thereof may equally well be used, magnesium being especially suitable for obtaining pure products. A lattice work 3 consisting of a plurality of metal bands, generally of the same metal as the box 1 and being, for example, 5 mm thick, riveted together is provided and is, in operation, arranged within the anode box being held in place by the baked lower portion of the paste-like anode mixture. The outer frame assembly 2 and the lattice work 3 serve to reinforce the anode and at the same time to conduct the electric current necessary for the electrolysis.

40 The anode assembly comprising the anode box 1, the outer frame assembly 2 and the lattice work 3, together with the paste-like mixture with which the assembly is filled is suspended from a supporting frame 5 into an electrolysis bath 4 as shown in Figs. 1 and 2 through adjustable suspension means comprising pulleys 6, ropes 7 and hangers 8.

As shown in the drawings, the cathode comprises two comb electrodes 9, each of which consists of eighteen round iron bars, of for example, 2 cm. cross section arranged in a row and equally spaced, for example at 5 cm. intervals.

The comb electrodes 9 are arranged in front of and behind the anode assembly at a suitable distance therefrom. These cathodic electrodes are suspended into the electrolysis bath 4 in a way similar to the anode.

With the capacity specified above, the furnace may, for example, be 2,73 metres long, 2 metres wide and 0,8 metres high, the central depth of the electrolysis bath to be charged with the salt mixture to be electrolysed being about 0,45 metres.

65 It is necessary before commencing opera-

tion to prebake at least a portion of the paste-like mixture with which the anode is charged. The prebaking may be carried out in a separate baking furnace. Or instead, as stated above, the electrolysis bath 4 itself 70 may be utilized for the purpose in which case the bath is charged with coke as resistor, in place of the normal charge for the electrolysis, using graphite electrodes for anode and cathode. When the prebaking 75 comes to an end, the coke is taken out to introduce the normal charge afresh into the bath, and the graphite electrodes provisionally used are replaced by the electrodes according to the invention. 80 When the arrangement is ready for operation as shown in Figs. 1 and 2) the anode and cathode are connected to the electric current source (not shown) to start the electrolysis. As the electrolysis proceeds, box 85 1, the lattice 3 and the anode paste are consumed gradually from below. The metal from the box 1 and lattice 3 has little influence on the bath composition or the purity of the magnesium produced, many of 90 the chlorides formed being volatile or insoluble in the bath and the electrolysis conditions being calculated to deposit minimal quantities of impurities. At suitable time intervals, the paste is, therefore, replenished 95 from above and at the same time the anode assembly is lowered gradually by adjusting the hanger 8. Periodically, as required, the lowest strips of the frame assembly 2 are detached from the bottom of the anode 100 assembly and then connected again from above to the anode assembly, conveniently by bolts and nuts, while the lattice work 3 is, at suitable time intervals, extended upwards by connecting a new lattice work 105 thereto, also conveniently by means of bolts and nuts. The box 1 is conveniently built up from above, as required, by placing box sections of the appropriate dimensions on top of the uppermost part of the box. Preferably, the upper and lower edges of the box sections are adapted to engage by, for example half-lap joints.

While the anode assembly is gradually lowered, the paste contained therein is successively baked by the heat of the bath, which is preferably kept at about 750°C, so that the lower portion thereof which is to react with the nascent chlorine is thoroughly baked up to the desired degree.

In order further to illustrate the invention an example of the electrolytic production of magnesium according to the invention will now be given.

Example

Roasted magnesite (MgO) 43 Kg. was dried, pulverized and sieved through a 100-mesh screen. The fine powder was thoroughly mixed with 20 Kg. pitch oil (fixed carbon content 30%) at a temperature of 200°C 130

using an oil bath and a mixer. The paste thus obtained was then charged into the anode box described above which is 120 cm. long and 50 cm. wide, with a cross-section of 6,000 sq. cm. The height of one charge amounted to about 5 cm., and it was therefore necessary to charge the box a number of times to obtain the preferred height of about 45 cm. Next, in order to carry out the prebaking of the anode mixture, the furnace chamber was filled with coke and then the anode assembly is lowered into position (as shown in Figs. 1 and 2). Graphite electrodes were then placed at both sides of the anode assembly and connected to a direct current source using the charged coke as resistor, the initial baking then being carried out in about ten days, the baking temperatures being increased by 80°C per day until it was 550°C and thereafter by 100°C per day. The temperature distribution of the baked electrode at the final stage was as follows:

25	Distance from bottom cm	Temperature, °C							
		0	5	10	15	20	25	30	40
	Temperature, °C	750	640	510	415	370	305	255	120

These values were substantially the same as those observed in the electrolytic operation.

30 After the coke was removed, the furnace chamber was then filled almost full with 700 Kg of a charging mixture comprising about 30% Mg Cl₂ and nearly 70% NaCl, to which was added 100 gm of calcium fluoride. The electrolysis was then started using the arrangement shown in Figs. 1 and 2, using a direct current of 2,000 amp. and 13 volts, and

keeping the bath temperature at 750°C. As the electrolysis proceeds, the anode paste was gradually baked upwards. In the course of operation, the anode paste together with the anode box and the lattice work, were gradually consumed from below at a speed of 4.3 cm. per day. As the anode was consumed, it was constantly replenished from above. The temperature gradient of the anode in operation was measured, the following values being obtained:

50	Distance from bottom cm	Temperature, °C								
		0	5	10	15	20	25	30	35	40
	Temperature, °C	755	640	515	420	370	310	255	200	130

A sample taken from the baked portion of anode showed a composition comprising 55 85% MgO and 15% C. The specific resistance of the baked portion amounted to 2-
3x10⁻² ohm cm. and the dipping depth of the anode in operation was constantly kept at about 3 cm. As the cathode, a couple of 60 comb electrodes (shown in Figs. 1 and 2) were used, the current densities being about 6 amp./cm² with a dipping depth nearly 1 cm and 0.8 amp./cm² with such depth of 10 cm. It is to be noted that the rate of decrease in 65 the bath composition of magnesium chloride was observed to be only 0.05% per hour, in contrast to that of the prior process using the same bath composition and current conditions in which case the rate of decrease is 70 as high as 0.4% per hour. In other words, the process according to the invention may proceed in a substantially continuous manner virtually without any necessity to replenish the MgCl₂ from outside.

75 The metallic magnesium produced by the above process is of 99.9% purity, the impurities being for example Al, Fe, Cu and Si. The output of magnesium was 17 Kg per day, the current and energy efficiencies 80 amounting to about 80% and about 15% respectively. The generating gases at the anode were compared with those obtained according to the prior known processes in which a graphite anode is used, the follow-

ing values being obtained. The upper values show those obtained by the present invention, while the lower ones stand for those by the prior process:

Cl ₂ %	CO ₂ %	CO%	90
5-10	55-53	40-37	
95-98	3-1	2-1	

It will be seen that according to the present process the gases liberated contained only a very small fraction of chlorine, as the nascent chlorine liberated immediately reacts with the magnesium in the anode to form MgCl₂.

WHAT I CLAIM IS:

1. A method for the electrolytic production of magnesium by the electrolysis of a fused mixture comprising magnesium chloride and alkali metal and/or alkaline earth metal halides, in which the anode comprises a paste-like mixture of a carbonaceous substance and a magnesium compound capable of reacting with the chlorine formed in the electrolysis, said paste-like mixture being surrounded by a metal shell, both the paste-like mixture and the metal shell being built up from above as the anode is consumed from below by the electrolytic process.

2. A method as claimed in claim 1 in which the magnesium compound capable of reacting with the chlorine formed in the

- electrolysis is magnesium oxide, roasted magnesite or magnesium hydroxide.
3. A method as claimed in either of claims 1 or 2 in which the carbonaceous substance is one or a mixture of more than one of the following substances:—pitch, tar, pitch oil, natural and artificial graphite, powdered coke or powdered charcoal.
4. A method as claimed in any of claims 10 1-3 in which the ratio of the magnesium compound to the carbonaceous substance is within the range of 1:3 to 3:1 by weight.
5. A method as claimed in any of the preceding claims in which the magnesium compound and the carbonaceous substance are thoroughly mixed together at a temperature between 170-230°C.
6. A method as claimed in any of the preceding claims in which the voltage of the electrolytic current is between 10-20 volts.
7. A method as claimed in any of the preceding claims in which the anodic current density is between 0.2-1.0 amps per sq. cm.
- 25 8. A method for the electrolytic production of magnesium substantially as herein described with reference to the example.
9. Magnesium when produced by a method as claimed in any of the preceding 30 claims.
10. Electrolytic apparatus adapted for the production of magnesium according to a method as claimed in any of the preceding claims comprising an electrolysis bath, a cathode and an anode, in which said anode comprises a paste-like mixture of a carbonaceous substance and a magnesium compound capable of reacting with chlorine liberated in the electrolysis, said paste-like
- mixture being surrounded by a metal shell, 40 said metal shell being so constructed that it can be built up from above as it is consumed from below by the electrolytic process.
11. Apparatus as claimed in claim 10, in which said metal shell comprises an inner 45 lattice-like frame and is associated with an outer frame with upper and lower openings.
12. Apparatus as claimed in claim 11 in which said outer frame comprises a plurality of side members detachably secured together 50 to form a plurality of boxlike sections each surrounding the anode and disposed in succession along its length thus enabling the lowermost sections of the frame to be dismantled and further upper sections added as 55 the electrode is consumed by electrolysis.
13. Apparatus as claimed in claim 12 in which said inner lattice-like frame is also adapted in operation to be replaced by the addition of further lattice elements. 60
14. Apparatus as claimed in any of claims 11-13 in which said metal shell consists essentially of a ferrous alloy, aluminium or an alloy thereof, or magnesium or an alloy thereof. 65
15. Electrolytic apparatus for the production of magnesium substantially as herein described with reference to the drawings.
16. Magnesium whenever produced in an apparatus as claimed in any of claims 10-15. 70

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825,872

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3 SHEETS

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the Original on a reduced scale.
SHEET 1

Fig 1

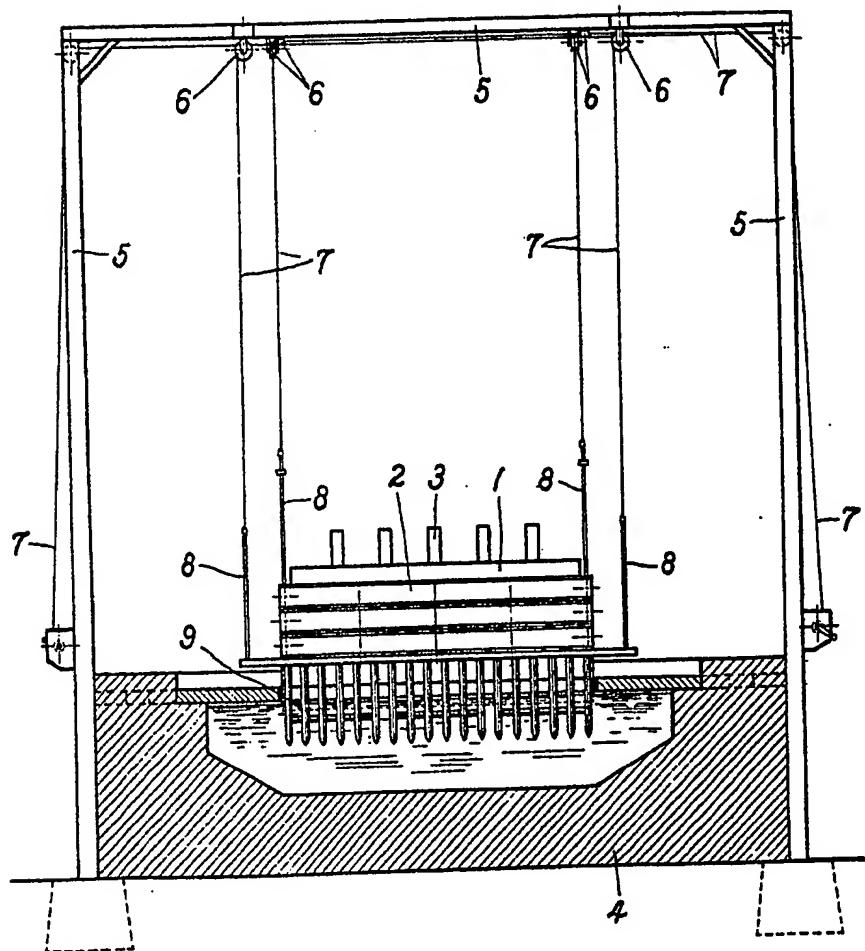
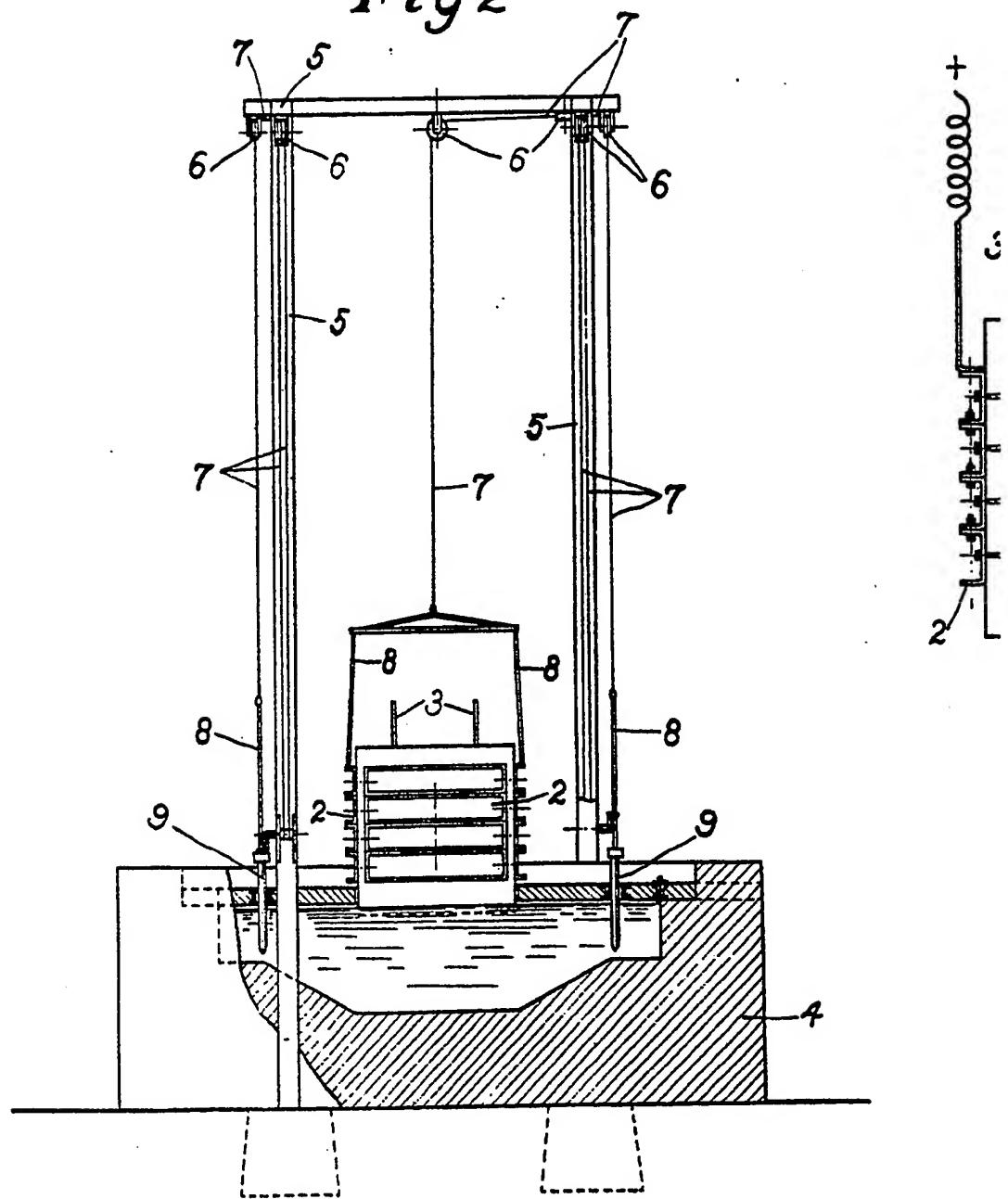


Fig 2



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3 SHEETS

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SHEETS 2 & 3

Fig. 3.

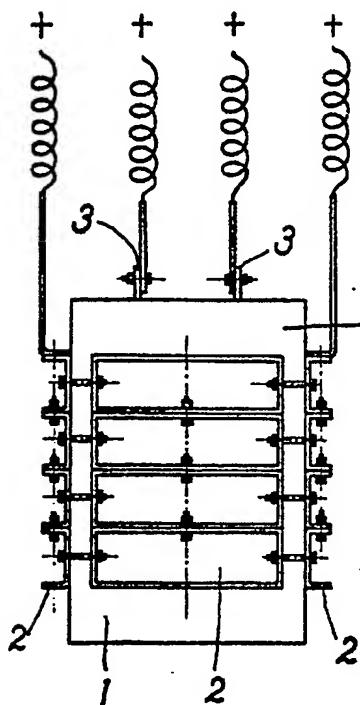


Fig. 4.

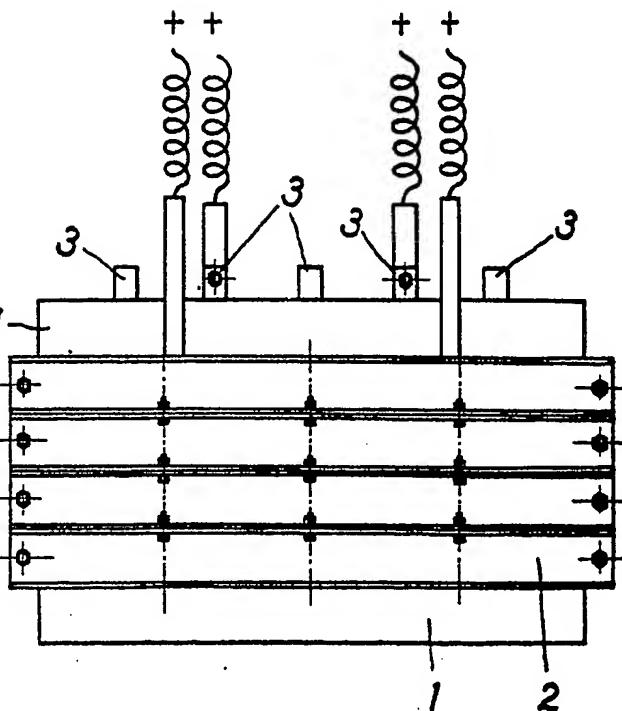
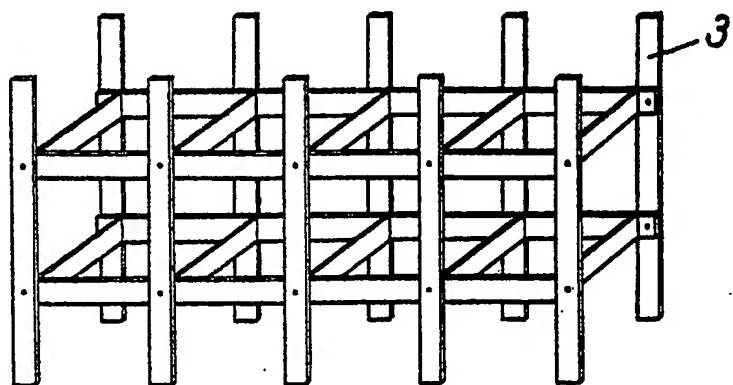


Fig. 5.



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SHEETS 2 & 3

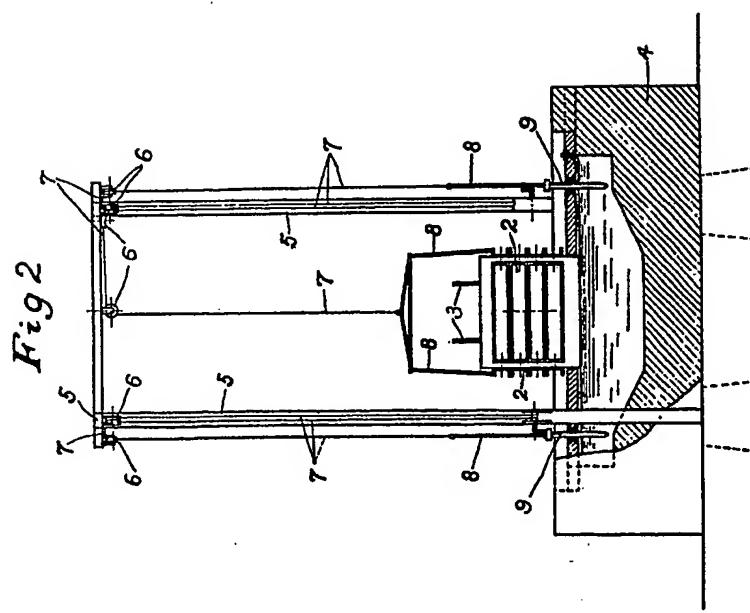


Fig. 3.

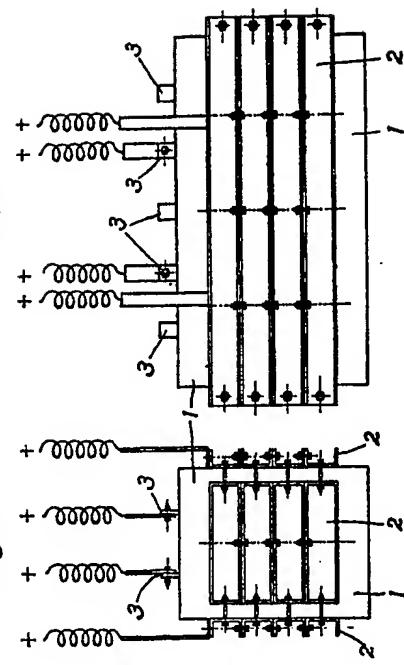


Fig. 4.

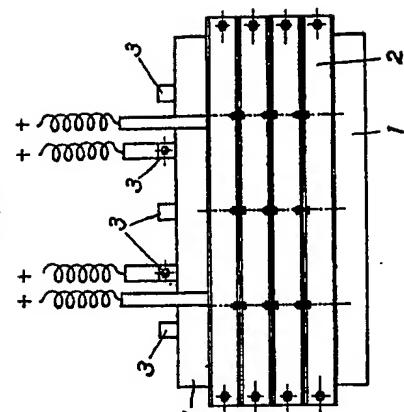


Fig. 5.

